Bio-Inspired Multi-gradient Structure Surfaces for Water Collection/Repellency

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ABSTRACT

Biological surfaces with micro- and nanostructures display unique wetting functions. Inspired by spider silk that collects water through a combination of multiple gradients, the bioinspired fibers are fabricated to achieve the water collection in efficiency. Inspired by butterfly wing and lotus leaf with micro- and nanostructures that repel water, the gradient structured surfaces are fabricated to realzie ultra water repellency and anti-icing abilities. These surfaces are opened a promising application.

Keywords: bioinspired, micro- and nanostructure, gradient, water collection, water repellency

1 INTRODUCTION

Natural creatures evolve their surfaces to endue various unusual abilities for survive in tough conditions through billions of years. Inspired by features of biological surfaces, designing and fabricating smart functional materials have become a very promising field of research. Since some creatures show special wettability on biological surfaces, such as lotus, water skipper, rose, butterfly, cactus in desert, spider silk, rice leaf and desert beetle. inspired by biological unique wettability resulted from micro- and nanostructures of surface, the multifunctional materials can be designed and fabricated for promising applications such as water-collecting, anti-icing, anti-frosting, or anti-fogging properties for practical applications in aerospace, industry and so on.

2 WATER COLLECTION

Recently, a novel wettability property is revealed on spider silks[1], it is found that cribellate spider capture silks can change into a kind of unique microstructure from original periodic puffs alternative joints from a dry capture silk (Fig. 1A), which composed of random nanofibrils (Fig. 1B) along periodic main-axis fibres. The structures of nano-scale dimensions play an important role in water collection function (Fig. C). The wettability of spider silks is enhanced due to these highly hydrophilic nanofibrils, which is favorable for condensing water drops. Spider silks have the humidity sensitive properties and the structure of spider silks can be re-built in a higher humidity. It is interesting that the structure of spider silk changes when a dry spider silk is placed in a higher humidity. Figure 1B shows the SEM images of wet-rebuilt spider silk. We can see that wetted spider silk has a more obvious spindle-knots and joints structure. Both of spindle-knots and joints are composed of randomly nanofibrils. But there are some differences between spindle-knots and joints nanofibrils. The nanofibrils of spindle-knots show rough and random conformation, and these of joints form an anisotropic aligned surface. Comparing to the spindle-knots surface, joint structure is smoother. This structure features lead to form two driving forces, i.e., surface energy gradient and a difference in Laplace pressure. This is why the water drops can move directionally. The nano-scale interactions with structural simplicity but functional complexity make silks have desirable and highly tunable properties. People always want to get the artificial spider silks through large-scale fabrication, which have the same nature properties as natural spider silks.[1-2]

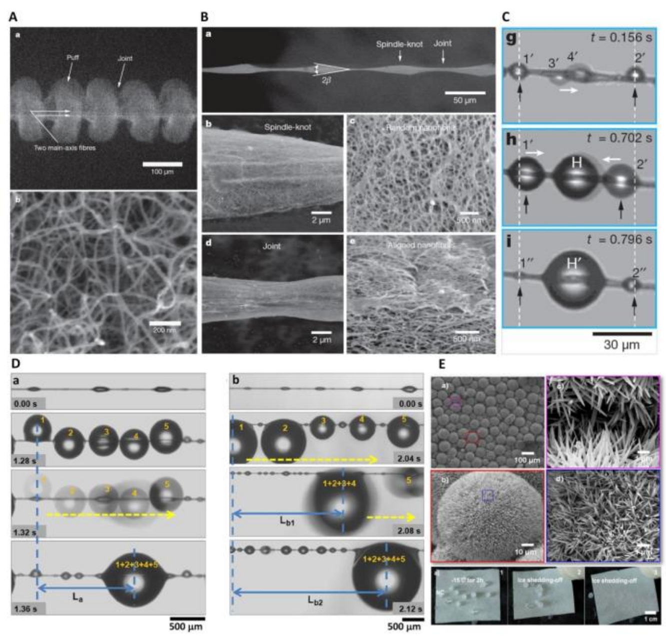

Figure 1. A-C) Scanning electron microscopy (SEM) images of dry spider capture silk with micro-"Puff-Joint" and nano-fibrils in Puff (A); Spindle-knot and joint are formed after wetting in mist, spindle-knot is composed of random nano-fibrils and Joint composed of aligned nano-fibrils (B); Optical images that tiny droplets move directionally toward spindle-knots from joint (C) (Nature,2010, 463, 640). D) Optical images that droplets move directionally via coalescence of droplets on as-designed gradient spindle-knotted fiber in a long range (Sci. Rep. 2013, 3, 2927). E) SEM images of flexible micro- and nanostructure (MN) polymer thin surface and de-ice ability of the surface (J. Mater. Chem. A, 2014, 2, 3312).

2.1 Bioinspired gradient fiber

we introduce typical methods to fabricate a series of artificial spider silks with spindle-knots and joints. A nylon fiber is firstly immersed into polymer solution and drawn out horizontally. After the nylon fiber is drawn out horizontally using a dip-coater machine, a cylindrical film forms on the uniform fiber surface. Due to the Rayleigh instability of the polymer solution, the film spontaneously breaks up into polymer droplets. The polymer drops became spindle-knots when being dried and formed spindle-knots and joints structure on the fiber. Optimizing condition, e.g., solution concentration and drawn-out velocity, this method can control the size of spindle-knots affecting the water collection ability. This method can be developed to fabricate different smart materials, e. g., bioinspired silks with multi-gradient and multi-scale spindle-knots, silkworm silk as the basic fiber can increase the biodegradability and biocompatibility of the water capture materials. Dip-coating method is simple and economical for fabrication of smart water collection materials. To use the Rayleigh instability technique and breath figure method, porous hump fibers can be fabricated successfully. The size and distribution of the pores can be controlled by changing the resin reaction conditions[3]. A variety of hump fibers with smooth, less porous, homogenous porous, gradient porous and dented micro-structures can be achieved. A carbon fiber is immersed in the resin solution (epoxy E-44 and diethylenetriamine mixed in the ratio of 10:1) and fabricated by dip-coating method. Due to the viscosity of solution increasing with the reaction time, it results in a different morphology of the bioinspired fibers. At 5 min, the surface is smooth because of evaporation of the solvent after a shot reaction time. At 10 min, the viscosity increases and the condensed water droplet is immobilized on the center of bead. Large micropores appear on the bead. After 15 min, the epoxy solution changes into a gel and makes the condensed water droplets hard to move. It results in a homogenous micropore distribution. After more reaction time, like 20 min, the sinking of condensed water droplets is limited due to the high viscosity, which leads a roughness gradient structure. Above 20 min, some dented areas are formed, as the condensed water droplets coalesce. Besides reaction time, the reactive humidity is also a factor to influence the porous structure. This porous materials have a variety of applications, e.g. biosensors, membranes, microreactors and devices. This is also a novel development for dip-coating method. The spindle-knot structure gives a broader perspective to design bioinspired materials. Compared with other methods, such as template-based synthesis, vapor-phase synthesis, solution-phase deposition and coaxial electrospinning, this simplicity and scalability of method allows rapid and easy large-scale fabrication.. Coaxial electrospinning (co-ESP) method can be used to fabricate various microscopic core-shell or tubular fibers with various materials. A sprayable outer fluid imprints a series of heterogeneous beads, and the spinnable inner fluid forms the centric fiber. The components of the inner and outer fluids should be controlled to form the bead-on-string hetero-structured fibers with tunable compositions. The spinnable inner fluid with high viscosity and the sprayable outer fluid with low viscosity combine and work through the inner and outer needle, respectively. Then bead-on-string hetero-structured fibers are collected on the aluminum foil. For the preparation of these bead-on-string hetero-structured fibers process, two fluids of inner/outer can't be miscible. The electrohydrodynamic process can prevent them from mixing at a short-time. The spinnable outer fluid with low viscosity is hard to envelope the inner fluid if using an immiscible solvent system. So we can't use two fluids easily separating in the jetting process to fabricate the bead-on-string hetero-structured fibers. The other effect factors to formation of bead-on-string hetero-structured fibers are the flow rate of the inner fluid. If it is too high, the spindle-knots structure decreases evidently or even disappear. However, if it is too low, the fluid is difficult to be shaped and drips from the nozzle. Increasing the inner fluid makes the decrease of the relative content of outer fluid, which will result in the decreasing of spindle-knots structure. In this design, the surface energy difference is considered. As described above, these two fluids should be miscible. However, we can manipulate the interface action by choosing appropriate solute components. The viscous drag force exerted by the inner fluid can be mitigated by the outer polymer with higher surface energy and inner polymer with lower surface energy. During the electrohydrodynamic jetting process, the outer polymer is conducive to the spontaneous Rayleigh break-up. In addition, the higher surface energy component can prevent the lower energy fluid wetting and adhesion during the solvent evaporation. This is a facile and powerful method to prepare novel bioinspired artificial spider silk fibers. It opens the field of electrohydrodynamic jetting to a much wider range of surface chemistries and applications. The method is simply and it offers a possibility to quickly fabricate 1-dimensional hetero-structured fiber materials on a large scale.

Learnt from the nature, bioinspired materials are fabricated to realize the water-collection ability by mimicking the micro-/nanostructure features of spider silks. In our previous studies, bioinspired artificial spider silk fibers are fabricated into periodic spindle-knots by dip-coating and coaxial electrospinning method. However, the dip-coating method is limited because of its discontinuity. We can't obtain a very long length of fiber using this method with a single 'immersing-in/drawing-out' operation. And it is hard to get a single bioinspired fiber by electrospinning method. So it requires us to find a new method to fabricate durable and inexpensive bioinspired artificial spider silk fibers and make the bioinspired material applied in large scale practical applications. Here, we introduce another method named fluid-coating method to continuously fabricate periodic spindle-knots on nylon fibers on a large scale. In order to avoid gravity-induced liquid flow, a nylon fiber is fed horizontally through a polymer solution reservoir. The fiber is fixed with one end connected to a rolling motor to drag the fiber through the polymer solution reservoir. Two capillary tubes are used to guide the fiber. When the fiber is steadily drawn out of the reservoir at a given velocity, the polymer solution is coating onto fiber surface at the end of the capillary tube. A charge coupled device (CCD) camera is used to record the whole fabrication process. These investigations demonstrate that using fluid coating method can fabricate the bioinspired artificial spider silk fibers with the structure similar to the spider silks. The fluid coating on fiber has been studied for a long time as a very common method. The applications of fluid coating range the improvement of the mechanical properties of fibers, e.g., using copper fibers, carbon fibers or fishing line fiber as the basic fibers, to the corrosion protection of metal wire, even includes simply make candles. Using this method, we should consider how to control the film thickness under this fabrication conditions. The viscous force makes the liquid move with the fiber. The force of the surface tension tends to drive the liquid back to the solution reservoir. The ratio of these two opposing forces largely affects the film thickness. The capillary number (Ca) can be described as follows: $C_a=\eta V/\gamma$, where η, V and γ are respectively the solution viscosity, the fiber drawing velocity and the surface tension of the solution. When the polymer solution is given, the solution viscosity and surface tension can't be changed. The coating behaviors base on the different drawing velocities to change. At the low velocities, the dynamic meniscus is stable and the film thickness generally obeys the Landau, Levich, Derjaguin (LLD) theory, called as the 'viscocapillary region'. When increasing the drawing velocity, the thickness of coated film also increases accordingly. At a very high velocity, it is important to consider the effect of inertia. We call the regime as the 'viscoinertial regime'. In this condition, it is unstable for the dynamic meniscus. The fluid-coating method can be used to fabricate bioinspired fibers with spindle-knots and joints on a large scale. These durable bioinspired artificial spider silk fibers can be applied in water collection, directional transport of liquid droplets. Designing structural features of the fiber surface can obtain novel functional fibers, e.g., directionally driving and intelligent catching and releasing. Chemical components heterogeneous or temperature responsive comply selective driving. Some light, pH, or thermal stimuli molecules modified on the fiber surfaces can also control the moving direction of water droplets. Slope and curvature effect achieves the stronger collection and higher-efficient liquid transportation along the fiber. In addition, the smart bioinspired functional fibers with unique wettability can be segmented swelling and shrinking with the environmental reversibility. The various fabrication methods of functional fibers provide a great guarantee for its wide range of applications.

2.2 Functions of water collection

In our previous studies, we successfully reproduced these structural features on bioinspired artificial spider silks. This material offers new insights in designing water collection materials. Here, we introduce how the fabrication conditions affect the geometric parameters of the spindle-knots and further the size affects the water collection ability. The spindle-knots/joints structures can be fabricated under an optimized condition and the size effect of the spindle-knots on the water collection ability.

It can clarify the effect of spindle-knot size on water collection ability. Three bioinspired artificial fibers with four spindle-knots and a uniform fiber are tested under the same fog flow and recorded by CCD in the same distance. The total volume of all the water droplets on the section of bioinspired artificial fibers at different collection time. At ~ 12 s, the bioinspired artificial fiber with the largest spindle-knots has collected ~ 35 nL, while it has only collected about 3 nL of water on the uniform fiber. It indicates that the spindle-knots size affects water collection ability and bioinspired artificial fibers collect more water than smooth fibers at the same condition. The interesting investigation shows that the water collection ability keeps step with the size of spindle-knots. These investigations show that we can evaluate the water collection ability of bioinspired artificial spider silks with different spindle-knot sizes. Using dip-coating method, we can fabricate the bioinspired artificial fibers with different sizes by controlling the solution viscosity, fiber drawing velocity and solution surface tension. In addition, the bioinspired silks with multi-gradient and multi-scale spindle-knots are fabricated via dip-coating Rayleigh instability technique and a water droplet template method. These investigations show that we can control to fabricate periodic spindle-knots on bio-inspired artificial spider silks. Based on these fabrication methods, the bioinspired artificial fibers with different spindle-knots sizes are applied in collecting fog, by quickly transporting, the condensed water droplets away and free the original place for a new cycle of condensation.

2.3 Rreversible directional driving

Liquid transport on surface is considerably significance in applications, e.g. fog harvesting, the design and operation of microfluidic, filtration, integrated DNA analysis devices and condensers. Liquid transport can be achieved by chemical method, thermal, and electrochemical methods. Inspired by the spider silks, a series of artificial gradient fibers is fabricated by designing chemical compositions and surface nanostructures. Except for design of smooth and rough spindle-knot on fiber, a kind of smart fiber is designed by using the N-isopropylacrylamide (NIPAAm) polymer with the temperature-responsive hydrogels. The spindle-knots surfaces on fibers are characteristics of the curvature, roughness and changeable wettability as well.

The tiny water droplets can be manipulated reversibly in directions movement toward or away from the spindle-knots in a certain of humidity by changing temperature (above or below lower critical solution temperature (LCST) of polymer). The block copolymers of PMMA-b-PNIPAAm (PMMA: poly(methyl methacrylate)) are synthetized by using Atom Transfer Radical Polymerization (ATRP) method to obtain temperature-responsive wettability effect. The water contact angles on PMMA-b-PNIPAAm surface can be changed with the temperature. It indicates that the wettability can be switched via a conformational change of the NIPAAm molecular chain at low/high temperatures. Using dip-coating method, the polymer solution is taken place with PMMA-b-PNIPAAm solution. The wettability of fiber surface is controlled by LCST because of PMMA-b-PNIPAAm along with the fiber. The forces from grandients of surface determine water droplet movement[4].

2.4 Directional transport of droplet

Intergated by the natural biological surfaces, such as the beetle's back, cacus and spider silks, a novel design to fabricate a spindle-knot structure via a special dip-coating method, which breaks the limit of water transport distance. From the fabrication method, the dip-coating is different from the common one. A uniform nylon fiber fixed on a support is soaked into a polymer solution with an angle to the horizontal line and then drawn out at a given velocity. This results in the sizes of the spindle-knots decreasing gradually[5]. Due to the angle to horizontal liquid level, the solution film on the fiber is obvious non-uniform to form the different size spindle-knots. This gradual structure produces a unique water directional movement channel, which breaks the limit of distance between two spindle-knots. The water droplet is directionally moving across four gradual spindle-knots in distance of ~ 5.0 mm during 130 s. There are three factors to drive the water droplets directional movement along the gradient fiber base on the research, including capillary adhesion, different in Laplace pressure on the gradual spindle- knots and drops coalescence release energy, respectively. At the first state, by the cooperation of surface energy in gradient and Laplace pressure in different, the tiny water droplets are driving toward spindle-knots. With the coalescence of tiny water droplets, a bigger water drop transports towards bigger spindle-knot for a stable condition due to the forces of different in Laplace pressure along the gradient spindle-knots and drops coalescence release energy at the second state. At the third state, water droplet hanging between two spindle-knots tends to slide from the smaller spindle-knot to bigger one because of capillary adhesion force difference. Multi-level cooperations of three forces drive micro-drops fast transport for a long distance. This creative bioinspired material realizes not only the water collection but also water transport. This novel material has many potential applications in fluid controlling and aerosols systems.

3 WATER REPELLENCY

Otherwise, biological surface such as plant leaves and butterfly wings display water repellency[6]. The suspending of microdroplets on a fresh lotus leaf is attributed to a gradient of wettable MNs along the exterior surface of papillae including nanohairs. The directional water repellency is achieved on wings of butterflies due to a flexibly oriented MN on wing. Also the MNs of wing generate low-temperature superhydrophobic properties. These biomimetic surfaces open the excellent water shedding-off/anti-icing properties. Investigations pave the promising future into micro-devices with the micro-fluid controlling and liquid transport, and also water collection in efficiency, and functions of anti-icing/ice-phobicity

Inspired by water repellcncy of butterfly wing with ratchet structures, a robust anti-icing and icephobic surface is fabricated by mechanical method and nanotechnoloty, which is composed of cooperative micro/nanostructures. The MN surface display excellent anti-icing and ice-phobicity, rather than that of individual nanostructures or microstructures, or smooth. With this design, the MN-surfaces generate a longer delay time of ∼ 7200 s to hold back the ice formation at a subzero temperature of –10 °C. Furthermore, A strong anti-ice property of nanohairs over micro-ratchet surfaces is observed. A long freezing delay ofmore than ~185 min is achieved for a droplet on the nanohairs over ratchet structure with a period of ~290 mm under -10°C, which is attributed to the effective cooperation of the nano- and microstructures.[7-8] In addition, a flexible MN thin polymer surface, similar to MN structures of lotus leaf, it also displays excellent de-ice ability[9] (Figure 1E).

In summary, inspired by biological unique wettability resulted from micro- and nanostructures of surface, the multifunctional materials can be designed and fabricated for promising applications such as water-collecting, anti-icing, anti-frosting, or anti-fogging properties for practical applications in aerospace, industry and so on.

REFERENCES

[1] Y. Zheng, et al., Nature 463, 640, 2010.
[2] X. Tian, et al., Adv. Mater. 23, 5486, 2011.
[3] Y. Hou, et al., Chem. Commun. 49, 5253. 2013,
[4] S. Feng, et al., J. Mater. Chem. A 1, 8363, 2013.
[5] Y. Chen, et al., Sci. Rep. 3, 2927, 2013.
[6] H. Mei, et al., Soft Matter 7, 10569, 2011.
[7] P. Guo, et al., Adv. Mater. 24, 2642, 2012.
[8] P. Guo, et al, Nanoscale 6, 3917, 2014.
[9] .L. Wang, et al, J. Mater. Chem. A, 2, 3312, 2014.